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(54) IMPROVEMENTS IN OR RELATING TO POLYESTERS

(71) We, HOECHST AKTIENGESSELLSCHAFT, a German Body Corporate, of 6230 Frankfurt/Main 80, Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the preparation of branched polyesters and novel resins derived therefrom with a narrow molecular weight distribution.

Molecular weight and molecular weight distribution are important features in characterising polymers. When describing the molecular weight, it is necessary to use, in general, two numerical averages of the molecular weight, the weight average \bar{M}_w

and the number average \bar{M}_n of the molecular weight. The quotient of the two averages

\bar{M}_w/\bar{M}_n can be used as a measurement of the breadth of molecular distribution. For a uniform compound it is 1, but for polymers it is always greater than 1, and for technical polyolefins it is e.g. about 6. It becomes particularly great in the case of polycondensates prepared by polycondensation of compounds of varying functionality. A polycondensate prepared, for example, from a dicarboxylic acid and a trihydric

alcohol has a very low \bar{M}_n and a very high \bar{M}_w at the so-called "gel point", i.e. at the moment of gelatinisation or cross-linking of the reaction mixture. It is also very non-uniform even before the gel point.

Alkyd resins are polyester resins which are prepared by polycondensation of reaction participants of varying functionality. As a rule, dicarboxylic acids or their anhydrides are polycondensed in the presence of monocarboxylic acids with polyhydric alcohols of varying functionality at 180 to 270°C. The products thus formed, as is well known, have a very broad molecular weight distribution which ranges from the lowest possible molecular weights, namely those of unreacted monomers, to very high molecular weights of molecules which have a very high degree of branching and are already partially cross-linked. According to the theory of polycondensation of more than bifunctional components, this is inevitable and cannot be prevented. This molecular weight distribution has also been experimentally confirmed using gel permeation chromatography (GPC).

It is known that, in alkyd resins used for coating purposes, the preferred technical properties are affected in very different ways by the low-molecular and high-molecular portions. The low-molecular portions of alkyd resins cause "stickiness" of the films during hardening and affect the stability, hardness, viscosity, chemical resistance and other properties of the films. It has also been pointed out that the resin films would dry more quickly in the air and, in the hardened state, would not have the disadvantages caused by the low-molecular fractions, if these fractions could be removed. This is true not only of the purely air-drying alkyd resins, but also of those which are hardened by heat treatment, using a cross-linking agent, e.g. a melamine resin.

The very high-molecular portions contained in an alkyd resin cause high viscosity, poor compatibility with other polymers, poor flow properties of the films, a lack of gloss and unsatisfactory solubility properties. By removing both the high-molecular and the low-molecular portions from alkyd resins, the disadvantages caused by them could be eliminated and the alkyd resins could be considerably improved. However,

there is no fractionation method by which this could be carried out really economically.

According to one suggestion, alkyd resins with a reduced content of high-molecular portions are supposed to be obtained by preparing them in the presence of relatively large quantities of inert solvents. The advantages of the product obtained can be explained by this fact. However, it is not possible to eliminate the presence of low-molecular portions with the proposed process.

It has also been proposed to prepare alkyd resins for powdered coating agents by reacting dicarboxylic acids (but not their anhydrides), a monohydric alcohol and, optionally, a monoepoxide in one or more steps, at a temperature of less than 160°C, to form an intermediate product containing free carboxyl groups, said product then being further reacted with at least one polyhydric alcohol at 150 to 250°C. The esterification with the polyhydric alcohol should, according to this proposal, be effected at moderate temperatures, in order to keep the molecular weight low and the molecular distribution as narrow as possible. The alkyd resin thus obtained is reacted with an aminoformaldehyde resin to form a precondensate. However, this reaction represents a conventional condensation reaction which proceeds statistically, with the result that there is still a relatively broad distribution of molecular weights in the products.

Surprisingly, it has now been found that there is nevertheless a way of preparing polyesters, the molecular weight distribution of which is characterized by the substantial absence of very low-molecular and high-molecular portions.

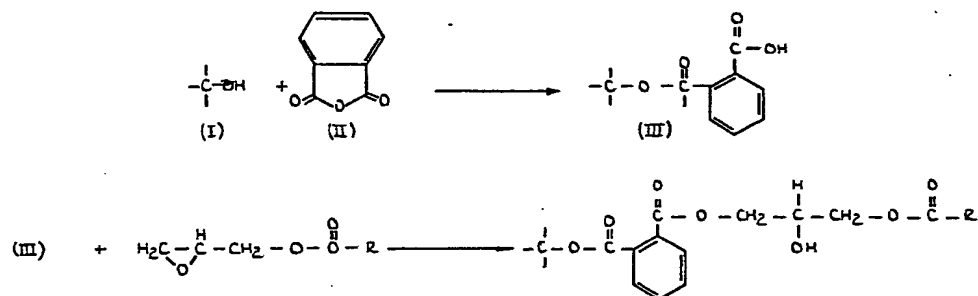
One aspect of this invention provides a process for the preparation of polyesters having a narrow molecular weight distribution wherein in a first step at least one polyhydric alcohol which is at least trihydric is reacted with up to one mol per hydroxyl group of at least one internal anhydride of a dicarboxylic acid at a temperature of up to 170°C to yield the corresponding dicarboxylic acid half ester as an intermediate, which in a second step is reacted with at least one monoepoxy compound which is a glycidyl ester or glycidyl ether to yield a corresponding diester of said dicarboxylic acid containing OH-groups, which diester containing OH-groups may be further alternately reacted a desired number of times with a) an internal anhydride of a dicarboxylic acid, and b) a monoepoxy compound to yield a branched product, and, where a glycidyl ether is used, the products are modified in a further step by reaction with at least one cross-linking agent.

The polyhydric alcohol may be employed in admixture with up to 50 mol% of one or more dihydric alcohols, although this is not preferred.

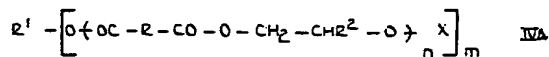
The internal anhydride a) and the monoepoxy compound b) are preferably the same as those employed in the first reaction step.

By this series of steps prior to cross-linking, branched e.g. star-shaped molecules may be obtained, the structure of which can be precisely fixed by the choice of reaction partners. It is possible to establish, by choosing the functionality of the polyhydric alcohol, how many branches (rays) a star-shaped end product will have. By means of the number of successive reaction steps it is possible to determine how long the rays of the star should be and whether they should have a carboxyl group or hydroxyl group in the end position. Moreover, the number of branch chains can also be affected by the molar ratios of reactants, as well as by the functionality of the polyhydric alcohol.

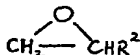
The equation below represents a reaction scheme for the first two reaction steps for an OH group of a polyhydric alcohol (I) used as starting material. In this case, o-phthalic anhydride is used as the dicarboxylic acid anhydride, and the glycidyl ester of a fatty acid is used as the epoxy compound.



The invention thus provides as a novel product a branched polyester having a narrow molecular weight distribution comprising units of the partial formula

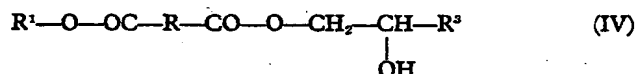


wherein R is an organic radical having 2 to 10 carbon atoms, R¹ is a residue of a polyhydric alcohol which is at least trihydric, each R² group independently is an organic group, X is hydrogen or an organic group, n is an integer and m is greater than 2, said polyester being substantially free of homologues of high molecular weight and having a molecular weight distribution substantially narrower than a branched polyester of the same mean molecular weight made by polycondensation of the reactants R¹(OH)_m, R(CO₂H)₂ and



or ester-forming derivatives of these.

The invention also relates to diesters with a narrow molecular weight distribution, which have the structural units



wherein:

R and R² have the meaning given above and

R² a CH₂-group substituted by an ester group having up to 18 carbon atoms.

Preferably R¹ is the residue of an at least trihydric alcohol with up to 10 C atoms or the residue of an esterified epoxy resin.

Suitable —R— groups in formulae (IV) and (IVa) are, for example, aromatic, saturated or olefinically unsaturated aliphatic or cycloaliphatic hydrocarbon groups which may optionally carry at least one halogen substituent, such as chlorine or bromine.

The resins of the invention have in general ratios of \bar{M}_w/\bar{M}_n in the range from 1.1:1 to 1.3:1, while the conventional resins in general have a ratio in the range from 1.8:1 to 2:1. The narrow molecular weight distribution of the products can be proved simply and elegantly using gel permeation chromatography.

The properties of the products may be varied within a broad framework by means of the reactants used and the number of successive reaction steps.

As the polyhydric alcohol, any such alcohol can be used, regardless of its chemical constitution. Naturally, those chiefly used will be the ones which are conventionally used in the preparation of polyester resins and which are available on an industrial scale, such as glycerol, pentaerythritol, dipentaerythritol, trimethylolethane, trimethylolpropane, ditrimethylolpropane, sorbitol; dihydric alcohols include ethyleneglycol, propyleneglycol or neopentylglycol. It is also possible to use as the polyhydric alcohol compounds prepared, for example, by reacting a polyepoxide with carboxylic acids, for example esterified aliphatic or aromatic epoxy resins, such as reaction products of diphenylolpropane and epichlorohydrin with monocarboxylic acids such as acrylic, methacrylic, acetic acid or the like.

Dicarboxylic acid anhydrides which may be used include o-phthalic anhydride, naphthalene-1,2-dicarboxylic anhydride, maleic anhydride, endomethylenetetrahydrophthalic anhydride, hexachloroendomethylenetetrahydrophthalic anhydride and succinic anhydride.

As epoxy compounds for use in the second step or stage b) as appropriate, glycidyl esters and glycidyl ethers are used e.g. the glycidyl esters of saturated and unsaturated synthetic or naturally occurring fatty acids, of acrylic or methacrylic acid, or of aromatic monocarboxylic acids, such as benzoic acid. Glycidyl ethers which may be used include the glycidyl ethers of phenols, and they may be substituted in various ways. The proportion used is appropriately equimolar to that of the free carboxyl groups of the half ester formed in the first step.

The initial polyesters prior to cross-linking are advantageously prepared, in all the steps, at temperatures of up to 170°C, preferably between 80 and 160°C. At these

temperatures, undesirable side reactions, such as interchange of ester radicals, etherification or esterification by the reaction of a carboxyl group with a hydroxyl group, virtually do not occur. As a result of reactions involving the interchange of ester radicals, for example, monocarboxylic acids could be liberated again and the advantage obtained by the reaction scheme of the invention would be cancelled out. The reaction time may vary depending on the choice of starting materials and other reaction conditions. It may be at least one hour.

It may occasionally be appropriate to prepare the products in the presence of a suitable catalyst which e.g. accelerates the reaction of a glycidyl group with a carboxy group. For this purpose, as is well known, amines, especially tertiary amines, may be used, such as mono-, di- and trialkyl or alkylarylamines, e.g. triethylamine. Moreover, cationic catalysts, particularly alcoholates such as alkali metal methoxides, e.g. sodium or potassium methoxide, are also suitable.

The quantity of catalyst is generally between 0.01 and 0.5% by weight of the total mixture, preferably between 0.05 to 0.2%.

An important advantage of the process according to the present invention, as compared with conventional polycondensation processes, consists in the shorter preparation times of each step and the relatively low temperatures, which means that a lower expenditure of energy is required. In addition, the fact that substantially no cleavage products are liberated represents a considerable simplification.

The polyesters with a narrow molecular weight distribution can be used for many of the applications for which polyester resins have been proposed. A number of advantages over corresponding products prepared in the conventional manner are obtained. In the preparation of coatings, these advantages at least sometimes include one or more of the following: very good flow properties, rapid hardening, great hardness of the hardened films combined, with good elasticity, good adhesion properties, excellent chemical resistance brought about by the optimal cross-linking properties, very good storage stability and compatibility with other polymers, caused by the absence of portions with high molecular weights, and very favourable solubility.

The intermediate polyester products may be used as the sole alcohol component in the preparation of polyesters or alkyd resins or as an additional condensation component, to restrict the molecular weight distribution of such a product to some extent.

The products may be used alone, particularly if they are air-drying products derived from glycidyl esters. However, they can also be used as mixtures with other polymers, e.g. with amine resins such as melamine, urea, guanamine resins or furan resins. If the products are not air-drying, it is appropriate to add cross-linking agents, e.g. the above-mentioned resins, or isocyanates.

If the products are prepared from glycidyl esters of unsaturated fatty acids, such as soya bean oil fatty acid, linseed oil fatty acid or cottonseed oil fatty acid, air-drying alkyd resins are obtained which, in addition to the advantages already described, also have relatively low viscosities. Such products can advantageously be modified with the glycidyl esters of aromatic monocarboxylic acids, such as benzoic acid, and/or glycidyl ethers of phenols, and such products are often preferred as are the products modified by glycidyl esters of unsaturated fatty acids.

Cross-linking can be effected by reacting the initial polyester with cross-linking agents, e.g. amine resins such as melamine, guanamine or urea resins or polyisocyanates or blocked polyisocyanates.

If glycidyl esters of aromatic monocarboxylic acids or glycidyl ethers of phenols are used, solid comminutable synthetic resins are obtained, which may be used as powder lacquers. In this case, the absence of low molecular portions represents an especial advantage, because, as is well known, the storage properties or blocking, resistance of coating powders are very disadvantageously affected by these low-molecular portions. At the same time, the powder coatings demonstrate good flow properties, which can be explained by the absence of high-molecular portions.

The powder lacquers appropriately have a particle size of up to 100, preferably from 50 to 70 μ .

The preparation of individual products according to the invention is described in the following Examples.

Unless otherwise stated, the properties or characteristics of the products were determined as follows: acid number according to DIN 53 183, OH number according to DIN 53 240, viscosity in the Ubbelohde viscosimeter and baking residue according to DIN 53 182.

The gel permeation chromatograms of the products prepared according to the invention demonstrate the advantages achieved according to the invention, over corresponding products prepared in the hitherto conventional manner. All the gel

chromatograms were taken with an analytical gel chromatograph of Messrs. Waters, Framingham, Massachusetts, USA, which was fitted with a set of columns particularly suitable for separating even relatively low-molecular fractions, this set of columns being based on a gel consisting of styrene, cross-linked with divinyl-benzene. The apparatus comprised eight 3-foot columns with an internal diameter of 0.95 cm, made by Messrs. Waters. As the calibrating substance, polystyrene was used, its molecular weight representing the "calibrating standard", and tetrahydrofuran was used as eluant.

In the gel chromatograms illustrated in Figures 1—12 the symbol Δn represents the difference in refractive indices between that of the solution leaving the chromatograph and that of the pure solvent. Δn is recorded in a logarithmic scale. V_E represents "elution volume", i.e. the quantity of liquid which leaves the gel chromatograph after passing through it. M represents molecular weight.

The direction of the arrow below the abscissa is from right to left, because the high-molecular portions leave first and the low-molecular portions are not obtained until the end.

Example 1

In a round-bottomed flask fitted with stirrer, reflux condenser and dropping funnel, 34 parts of pentaerythritol are heated with 148 parts of *o*-phthalic acid anhydride in 50 parts of white spirit (boiling range 145/200) and 10 parts of xylene for 2 hours in an inert gas atmosphere (CO_2 or nitrogen), with constant stirring, to 140°C. A mixture of 271 parts of the glycidyl ester of conjugated soya bean oil fatty acid and 58.5 parts of glycidyl *p*-tert.-butylbenzoate is then added in such a way that the temperature of the mixture does not exceed 160°C. Subsequently the mixture is heated to 160°C until a sample taken from the mixture is found to have an acid number of less than 2.

A further 148 parts of *o*-phthalic acid anhydride are added at 140°C and the product is again reacted with 271 parts of the glycidyl ester of conjugated soya bean oil fatty acid and 58.5 parts of glycidyl *p*-tert.-butylbenzoate. This alternating reaction with *o*-phthalic acid anhydride and the glycidyl ester is repeated twice more 2000 parts of an alkyd resin are obtained, which may advantageously be used to prepare air-drying lacquers.

Characteristics: acid number 3.4, OH number 47, viscosity (50% in a mixture of white spirit 200 and xylene (volume ratio 5:1)) 1.60 poise.

The gel chromatogram of the product is shown as a continuous curve in Fig. 1.

Comparison to Example 1

In a flask provided with stirrer, reflux condenser and water separator, a mixture of 17 parts of pentaerythritol, 296 parts of *o*-phthalic acid anhydride, 184 parts of glycerol, 89 parts of *p*-tert.-butylbenzoic acid, 421 parts of conjugated soya bean-oil fatty acid and 50 parts of xylene are heated to 210°C in an inert gas atmosphere. At this temperature the mixture is polycondensed with the continuous removal of the reaction medium by azeotropic distillation with xylene, until the acid number is less than 6.1000 parts of an alkyd resin are obtained which are then dissolved in 670 parts of a mixture of white spirit (145/200) and xylene (5:1 parts by vol).

Characteristics: baking residue 60%, acid number 5, OH number 24, viscosity (50% in a mixture of white spirit 200 and xylene, volume ratio 5:1) 34 poise.

The gel chromatogram of the comparison product is shown as the broken curve in Fig. 1.

Example 2

In a flask provided with stirrer, reflux condenser and dropping funnel, 63.5 parts of dipentaerythritol are stirred for 2 hours at 140°C with 222 parts of *o*-phthalic acid anhydride in the presence of 115 parts of xylene. 366 parts of a glycidyl ester of Versatic acid (registered Trade Mark) i.e. a branched chain synthetic fatty acid, are then added in such a way that the temperature of the mixture does not exceed 160°C. The mixture is left to stand at 160°C until the acid number is less than 2.766 parts of the product are obtained, which can be processed, e.g. with melamine resins or polyisocyanates, to form very hard glossy coatings. Characteristics: Baking residue 85%, acid number 1, OH number 135, viscosity (80% in xylene) 97.5 poise.

The continuous curve in Fig. 2 shows the gel chromatogram of the product.

Comparison to Example 2

Owing to its chemical structure, versatic acid esterifies only extremely slowly. For the comparison therefore, another branched-chain saturated fatty acid of more or less the same molecular weight was used, namely isononanic acid.

63.5 parts of dipentaerythritol, 222 parts of *o*-phthalic acid anhydride, 138 parts

of glycerol and 237 parts of isononanic acid are polycondensed at 200°C, according to the method of Comparison Example 1, in the presence of 50 parts of xylene, until the acid number is less than 5.700 parts of an alkyd resin are obtained. Characteristics: Baking residue 93%, acid number 4, OH number 110, viscosity (50% in xylene) 520 poise.

Fig. 2 shows the gel chromatogram of the comparison product as a broken curve.

Example 3

According to the method of Example 2, 67 parts of trimethylolpropane are reacted with 111 parts of *o*-phthalic acid anhydride, 120 parts of endomethylenetetrahydrophthalic acid anhydride, 250 parts of the same glycidyl ester as in Example 2 and 180.5 parts of a glycidyl ester of conjugated soya bean oil fatty acid, until the acid number of the product is less than 2.728 parts of a resin are obtained, which can advantageously be processed with melamine resins to form hard, glossy coatings.

Characteristics: Baking residue 100%, acid number 1.8, OH number 122, viscosity (80% in xylene) 110 poise. Fig. 3 shows the gel chromatogram of the product as a continuous curve.

Comparison to Example 3

67 parts of trimethylolpropane are polycondensed at 200°C with 111 parts of *o*-phthalic acid anhydride, 120 parts of endomethylenetetrahydrophthalic acid anhydride, 138 parts of glycerol, 158 parts of isononanic acid and 140 parts of conjugated soya bean oil fatty acid in the presence of 50 parts of xylene, until the acid number is less than 6.770 parts of the product are obtained. Characteristics: baking residue 94%, acid number 5.3, OH number 105, viscosity (80% in xylene) 305 poise.

Fig. 3 shows the gel chromatogram of the comparison product as a broken line.

Example 4

Using the method described in Example 2, 68 parts of pentaerythritol are reacted with 296 parts of *o*-phthalic acid anhydride and 433 parts of the glycidyl ester used in Example 2, in the presence of 150 parts of xylene, until the acid number of the product is less than 17. Subsequently 296 parts of *o*-phthalic acid anhydride and a further 433 parts of the above starting glycidyl ester are each added twice. 2405 parts of a product are obtained, which can be baked with melamine resins to yield very elastic and durable coatings. Characteristics: baking residue 94%, acid number 8.5, OH number 49, viscosity (80% in xylene) 79.5 poise.

The gel chromatogram of the product is shown as a continuous curve in Fig. 4.

Comparison to Example 4

68 parts of pentaerythritol and 482 parts of glycerol are polycondensed with 888 parts of *o*-phthalic acid anhydride and 826 parts of isononanic acid in the presence of 100 parts of xylene, at 210°C, until an acid number of less than 10 is attained. 2350 parts of a product with the following characteristics are obtained: baking residue 97%, acid number 9, OH number 45, viscosity (80% in xylene) 525 poise.

Fig. 4 shows the gel chromatogram of the comparison product as a broken line.

Example 5

33.5 parts of trimethylolpropane and 25.3 parts of pentaerythritol are reacted, as in Example 2, with 222 parts of *o*-phthalic acid anhydride, 214 parts of the glycidyl ester of isononanic acid and 117 parts of the glycidyl ester of *p*-tert-butylbenzoic acid. 612 parts of a product are obtained, which can very advantageously be processed e.g. with melamine resins or polyisocyanates, to form a coating. Characteristics: baking residue 100%, acid number 2, OH number 135, viscosity (80% in xylene) 72.5 poise.

Fig. 5 shows the gel chromatogram of the product as a continuous line.

Comparison to Example 5

33.5 parts of trimethylolpropane, 25.3 parts of pentaerythritol, 222 parts of *o*-phthalic acid anhydride, 138 parts of glycerol, 158 parts of isononanic acid and 89 parts of *p*-tert-butylbenzoic acid are polycondensed at 210°C in the presence of 50 parts of xylene, until an acid number of less than 5 is attained. 660 parts of a polycondensate with the following characteristics are obtained: baking residue 93%, acid number 4, OH number 120, viscosity (80% in xylene) 480 poise. Fig. 5 shows the gel chromatogram of the comparison product as a broken line.

Example 6

34 parts of pentaerythritol are reacted twice in succession, as in Example 2, each time with 148 parts of *o*-phthalic acid anhydride and 234 parts of the glycidyl ester of *p*-tert-butylbenzoic acid, until an acid number of less than 3 is attained. 798 parts of a solid grindable product which may be ground (or milled) are obtained, which can be cross-linked via its OH groups, e.g. with polyisocyanates. Characteristics: baking residue 100%, acid number 2, OH number 76, melting range 87—90°C.

Fig. 6 shows the gel chromatogram of the product as a continuous line.

Example 7

According to the method of Example 2, 34 parts of pentaerythritol are reacted twice in succession, each time with 148 parts of *o*-phthalic acid anhydride and with 150 parts of phenylglycidyl ether in the presence of 0.7 parts of triethylamine until the acid number is less than 1.332 parts of a solid, grindable product are obtained, which can be cross-linked via its OH groups, e.g. with polyisocyanates. Characteristics: baking residue 100%, acid number 0.4, OH number 156, melting range 40—43°C. Fig. 6 shows the gel chromatogram of the product as a broken line.

Discussion of the results obtained in Examples 1 to 7

As Figures 1 to 6 show, the molecular weight distribution of the compounds prepared according to Examples 1 to 7 is narrower and therefore superior to that of the comparison substances.

Example 8

In a flask fitted with a stirrer, reflux condenser and dropping funnel, 134 parts of trimethylolpropane and 294 parts of maleic acid anhydride are stirred for 3 hours at 130°C in the presence of 130 parts of xylene. 744 parts of glycidyl versatate are then added dropwise in such a way that the temperature of the reaction medium does not exceed 160°C. After the addition is complete, the mixture is maintained at this temperature until the following characteristics are obtained: baking residue 86%, acid number less than 1, OH number 148, viscosity (80% in xylene) 20 poise.

Figure 7 shows the gel chromatogram of the product.

Example 9

134 parts of trimethylolpropane, 333 parts of *o*-phthalic acid anhydride and 73.5 parts of maleic acid anhydride are reacted, in the presence of 130 parts of xylene, as in Example 8, with 744 parts of glycidyl versatate. A product with the following characteristics is obtained: baking residue 89%, acid number 4.4, OH number 140, viscosity (80% in xylene) 35.6 poise.

Figure 8 shows the gel chromatogram of the product.

Example 10

136 parts of pentaerythritol and 392 parts of maleic acid anhydride are reacted, in the presence of 160 parts of xylene, as in Example 8, with 992 parts of glycidyl versatate. A product with the following characteristics is obtained: baking residue 88%, acid number 2.8, OH number 153, viscosity (80% in xylene) 42.3 poise. Figure 9 shows the gel chromatogram of the product.

Example 11

136 parts of pentaerythritol and 294 parts of maleic acid anhydride are reacted in the presence of 120 parts of xylene, as in Example 8, with 670 parts of glycidyl versatate. A product with the following characteristics is obtained: baking residue 89%, acid number 14, OH number 170, viscosity (80% in xylene) 381.6 poise. Figure 10 shows the gel chromatogram of the product.

Preparation of lacquers

Example A

63.65 parts of the product obtained according to Example 6, coarsely milled (maximum particle size about 1 mm), are mixed in an extruder or kneader, at 80 to 100°C, with 27.25 parts of titanium dioxide, 7.7 parts of pyromellitic acid dianhydride and 1.4 parts of polyacrylate [Modaflow (registered Trade Mark), manufactured by Monsanto]. After cooling, a powder lacquer with a particle size of less than 100 μ , preferably up to 80 μ , is prepared from the hardened melt by breaking, milling and subsequent sieving of the powder obtained. The lacquer is applied to phosphatised sheets of steel in a *per se* known manner, by electrostatic spraying and is then baked

at 200°C for half an hour. A chemically resistant, stable coating is obtained, which meets the technical requirements of lacquers.

Example B

From the products of Examples 8 to 11, a lacquer was prepared by trituring 70 parts of the polyester resin obtained according to each Example with 50 parts of titanium dioxide, at 40 to 50°C, to form a paste. After cooling, 30 parts of melamine resin were added to the mass and, by adding xylene, the mixture was adjusted to have a flow time of 20 to 25 seconds in a DIN flow cup (4 mm). The lacquer was baked at various temperatures, each time for 30 minutes. The hardened coatings were tested for their technical lacquer properties. The values obtained are assembled in the following Table.

		TABLE			
Example		8	9	10	11
Baking temperature 130°C					
Pendulum hardness*		—	111	—	135
Gloss		110	114	—	112
Erichsen cupping mm.		9.5	8.9	—	7.2
Lattice cut test,** evaluation scale		0—0.5	0—0.5	—	1
Baking temperature 140°C					
Pendulum hardness		—	130	110	162
Gloss		114	120	114	107
Erichsen cupping mm.		8.8	8.3	7.2	6.1
Lattice cut test, evaluation scale		0	1	0—1	4
Baking temperature 150°C					
Pendulum hardness		—	163	141	164
Gloss		114	114	112	109
Erichsen cupping mm.		8.2	7.7	6.7	5.3
**DIN 53 151					
*DIN 53 157					

The values in the Table show that, according to all the Examples, lacquers with good properties are obtained. Moreover, Figures 7 to 10 show that the molecular weight distribution of the products obtained is narrow.

WHAT WE CLAIM IS:—

1. A process for the preparation of polyesters having a narrow molecular weight distribution wherein in a first step at least one polyhydric alcohol which is at least trihydric is reacted with up to one mol per hydroxyl group of at least one internal anhydride of a dicarboxylic acid at a temperature of up to 170°C to yield the corresponding dicarboxylic acid half ester as an intermediate, which in a second step is reacted with at least one monoepoxy compound which is a glycidyl ester or glycidyl ether to yield a corresponding diester containing OH-groups of said dicarboxylic acid, which diester containing OH-groups may be further alternately reacted a desired number of times with a) an internal anhydride of a dicarboxylic acid, and b) a monoepoxy compound to yield a branched product, and, where a glycidyl ether is used, the products are modified in a further step by reaction with at least one cross-linking agent.

2. A process as claimed in claim 1 wherein said first step is performed at a temperature between 80 and 160°C.

3. A process as claimed in either of claims 1 and 2, wherein said internal anhydride a) reacted with the product of the second step is the same as that employed in the first reaction step.

4. A process as claimed in any of the preceding claims wherein said monoepoxy compound b) reacted with the reaction product of the internal anhydride with the product of the second step is the same as that reacted in the second reaction step.

5. A process as claimed in any one of the preceding claims wherein said internal anhydride of the dicarboxylic acid is the anhydride of an aromatic dicarboxylic acid.

6. A process as claimed in claim 5 wherein said internal anhydride is phthalic anhydride.

7. A process as claimed in any one of the preceding claims wherein said polyhydric alcohol is trihydric.

8. A process as claimed in any one of the preceding claims wherein said polyhydric alcohol is employed in admixture with up to 50 mol% of one or more dihydric alcohols.

9. A process as claimed in any one of the preceding claims wherein the polyhydric alcohol is an esterified epoxy resin containing hydroxy groups.

10. A process as claimed in claim 9 wherein the polyhydric alcohol is an epoxy resin containing hydroxy groups and esterified with a monocarboxylic acid selected from acrylic acid, methacrylic acid, and acetic acid.

11. A process as claimed in any of the preceding claims wherein the monoepoxy compound is a glycidyl ester of a fatty acid.

12. A process as claimed in any of claims 1 to 10 wherein the monoepoxy compound is a glycidyl ester of acrylic acid, methacrylic acid or an aromatic carboxylic acid.

13. A process as claimed in claim 11 wherein said glycidyl ester is an ester of an unsaturated fatty acid which yields an air-drying reaction product.

14. A process as claimed in claim 13 wherein said unsaturated fatty acid is derived from soya oil, linseed oil or cotton oil.

15. A process as claimed in any one of claims 11, 13 or 14 wherein said glycidyl ester includes a glycidyl ester of a saturated fatty acid and optionally a glycidyl ester of an aromatic monocarboxylic acid whereby an alkyd resin reaction product of low viscosity is obtained.

16. A process as claimed in any one of claims 11, 13, 14, or 15 wherein the glycidyl ester additionally contains phenylglycidyl ethers to yield a solid product suitable for grinding.

17. A process as claimed in any one of claims 11 to 16 wherein the glycidyl esters and/or ethers are reacted in an amount substantially equivalent to the free carboxyl groups of the half esters obtained in the previous reaction step.

18. A process as claimed in any one of the preceding claims wherein the monoepoxy compound is reacted in the presence of a catalyst.

19. A process as claimed in claim 18 wherein the catalyst is a tertiary amine or a metal alcoholate.

20. A process as claimed in claim 18 or 19 wherein the catalyst is present in an amount of from 0.01 to 0.5% by weight, referred to the total solids content.

21. A process as claimed in claim 20 wherein the amount of the catalyst is in the range from 0.05 to 0.2% by weight.

22. A process as claimed in any one of the preceding claims wherein, when the monoepoxy compound is a glycidyl ester, the hydroxy groups of the polyester product is modified in a further step by reaction with at least one cross-linking agent.

23. A process as claimed in claim 22 wherein said cross-linking agent is at least one amine resin, isocyanate or blocked isocyanate cross-linking agent.

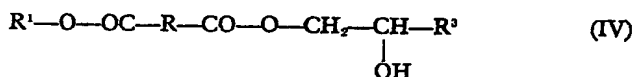
24. A process as claimed in any one of the preceding claims substantially as described herein.

25. A process as claimed in any one of the preceding claims substantially as described herein with reference to any one of Examples 1 to 7.

26. A polyester made by the process of any one of the preceding claims.

27. The product of curing the polyester product of any one of claims 13, 14, 22 or 23.

28. A dicarboxylic acid diester product of claim 1 having the formula



wherein:

R is an organic radical having 2 to 10 carbon atoms,

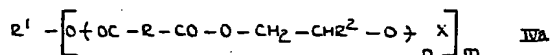
R¹ is a residue of a polyhydric alcohol which is at least trihydric,

R² is a CH₂-group substituted by an ester group having up to 18 carbon atoms.

29. An ester of claim 28 wherein said polyhydric alcohol has up to 10 carbon atoms or is an esterified epoxy resin.

30. An ester as claimed in claim 28 or 29 wherein R is a hydrocarbon radical having at least one chlorine or bromine substituent.

31. A branched polyester having a narrow molecular weight distribution comprising structural units of the formula



wherein:

R and R¹ are as defined in claim 28 and each R² group independently is an organic group,

X is hydrogen or an organic group,

n is an integer and m is greater than 2, said polyester being substantially free of homologues of high molecular weight and having a molecular weight distribution substantially narrower than a branched polyester of the same mean molecular weight made by polycondensation of the reactants R¹(OH)_m R(CO₂H)_n and



or ester-forming derivatives of these.

32. A polyester as claimed in claim 31, modified by being linked through the hydroxyl group thereof to the residue of a glycidyl ester of an unsaturated fatty acid or a glycidyl ester of an aromatic monocarboxylic acid.

33. A polyester as claimed in claim 31 wherein R² is a CH²-group substituted by an ester group of an air-drying fatty acid.

34. A coating composition comprising a polyester as claimed in any one of claims 26 to 35.

35. A coating composition as claimed in claim 34 which is a powder coating composition.

36. A coating composition as claimed in claim 34 or 35 having a particle size of at most 100 μ.

37. A coating composition as claimed in claim 36 having a particle size of from 50 to 70 μ.

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